We claim:

1. A photocatalytically-activated self-cleaning article of manufacture comprising:

a substrate having at least one surface; and

a photocatalytically-activated self-cleaning coating deposited over the surface of the substrate by a process selected from the group consisting of chemical vapor deposition, magnetron sputtered vacuum deposition and spray pyrolysis.

2. The photocatalytically-activated self-cleaning article of claim 1 wherein the photocatalytically-activated self-cleaning coating comprises a metal oxide selected from the group consisting of titanium oxides, iron oxides, silver oxides, copper oxides, tungsten oxides, aluminum oxides, silicon oxides, zinc stannates, molybdenum oxides, zinc oxides, strontium titanate and mixtures thereof.

3. The photocatalytically-activated self-cleaning article of claim 2 wherein the photocatalytically-activated self-cleaning coating ~~comprises~~ titanium dioxide selected from the group consisting of anatase titanium dioxide, rutile titanium dioxide, brookite titanium dioxide and mixtures thereof.

4. The photocatalytically-activated self-cleaning article of claim 1 wherein said photocatalytically-activated self-cleaning coating is at least 200 Angstroms thick.

5. The photocatalytically-activated self-cleaning article of claim 1 wherein said photocatalytically-activated self-cleaning coating is at least about 400 Angstroms thick.

6. The photocatalytically-activated self-cleaning article of claim 1 wherein said photocatalytically-activated self-cleaning coating is at least about 500 Angstroms thick.

7. The photocatalytically-activated self-cleaning article of claim 1 wherein said photocatalytically-activated self-cleaning coating has a photocatalytic reaction rate of at least 2 x 10^{-3} $cm^{-1}min^{-1}$.

8. The photocatalytically-activated self-cleaning article of claim 7 wherein said photocatalytic reaction rate is determined as the rate of removal of a stearic acid test film in the range of 100 to 200 Angstrom thick deposited over said photocatalytically-activated self-cleaning coating wherein said photocatalytic reaction rate is quantitatively determined as the slope of a curve formed by a plotting of a plurality of Fourier Transform Infrared Spectrophotometer measurements of the integrated intensity of carbon-hydrogen stretching vibrational absorption bands of the stearic acid test film versus an accumulated time of exposure of said photocatalytically-activated self-cleaning coating to ultraviolet radiation of a frequency within the range of about 300 to 400 nanometers provided by an ultraviolet radiation source positioned over said photocatalytically-activated self-cleaning coating and having an intensity of about 20 watts per square meter as measured at the surface of the photocatalytically-activated self-cleaning coating.

9. The photocatalytically-activated self-cleaning article of claim 8 wherein said ultraviolet radiation source is selected from the group consisting of a black light source and a UVA-340 light source.

10. The photocatalytically-activated self-cleaning article of claim 1 wherein the photocatalytically-activated self-cleaning coating is deposited directly over the substrate.

11. The photocatalytically-activated self-cleaning article of claim 1 further comprising at least one layer interposed between said photocatalytically-activated self-cleaning coating and the substrate.

12. The photocatalytically-activated self-cleaning article of claim 1 wherein said photocatalytically-activated self-cleaning coating comprises one layer of a multilayer stack of coatings deposited over the substrate and wherein the photocatalytically-activated self-cleaning coating is the uppermost layer of said multilayer stack.

13. The photocatalytically-activated self-cleaning article of claim 1 wherein said photocatalytically-activated self-cleaning coating comprises one layer of a multilayer stack of coatings deposited over the substrate wherein said photocatalytically-activated self-cleaning coating is a layer other than the uppermost layer of said multilayer stack.

14. The photocatalytically-activated self-cleaning article of claim 1 further comprising a sodium ion diffusion barrier layer disposed between the substrate and the photocatalytically-activated self-cleaning coating to inhibit migration of sodium ions from said substrate to said photocatalytically-activated self-cleaning coating.

15. The photocatalytically-activated self-cleaning article of claim 14 wherein the sodium ion diffusion barrier layer is deposited over the substrate by a process selected from

the group consisting of chemical vapor deposition, magnetron sputtered vacuum deposition and spray pyrolysis.

16. The photocatalytically-activated self-cleaning article of claim 14 wherein the sodium ion diffusion barrier layer is selected from the group consisting a crystalline metal oxide, an amorphous metal oxide and mixtures thereof.

17. The photocatalytically-activated self-cleaning article of claim 16 wherein the sodium ion diffusion barrier layer is selected from the group consisting of tin oxides, silicon oxides, titanium oxides, zirconium oxides, fluorine-doped tin oxides, aluminum oxides, magnesium oxides, zinc oxides, cobalt oxides, chromium oxides, magnesium oxides, iron oxides and mixtures thereof.

18. The photocatalytically-activated self-cleaning article of claim 17 wherein the sodium ion diffusion barrier layer is at least about 250 Angstroms thick.

19. The photocatalytically-activated self-cleaning article of claim 17 wherein the sodium ion diffusion barrier layer is at least about 400 Angstroms thick.

20. The photocatalytically-activated self-cleaning article of claim 17 wherein the sodium ion diffusion barrier layer is at least about 500 Angstroms thick.

21. The photocatalytically-activated self-cleaning article of claim 1 wherein the substrate is selected from the group consisting of glass, plastic, metal, enamel and mixtures thereof.

~~22. The photocatalytically-activated self-cleaning~~ article of claim 1 wherein said substrate is a glass substrate having a first major surface and an opposite major surface defined as a second major surface, the first major surface having a thin layer of a tin oxide diffused therein characteristic of forming a glass ribbon over a molten tin bath, at least one of the major surfaces having said photocatalytically-activated self-cleaning metal oxide coating deposited thereon.

23. The photocatalytically-activated self-cleaning article of claim 22 wherein the photocatalytically-activated self-cleaning coating further comprises a metal oxide selected from the group consisting of titanium oxides, iron oxides, silver oxides, copper oxides, tungsten oxides, aluminum oxides, silicon oxides, zinc stannates, molybdenum oxides, zinc oxides, strontium titanate and mixtures thereof.

24. The photocatalytically-activated self-cleaning article of claim 23 further comprising a sodium ion diffusion barrier layer disposed between the substrate and the photocatalytically-activated self-cleaning coating.

25. The photocatalytically-activated self-cleaning article of claim 24 wherein the sodium ion diffusion barrier layer is selected from the group consisting of tin oxides, silicon oxides, titanium oxides, zirconium oxides, fluorine-doped tin oxides, aluminum oxides, magnesium oxides, zinc oxides, cobalt oxides, chromium oxides, magnesium oxides, iron oxides and mixtures thereof.

26. The photocatalytically-activated self-cleaning ~~article of claim 22 wherein the glass substrate is~~ selected from

the group consisting ~~of a glass sheet and a continuous float~~ glass ribbon.

27. A method for providing a titanium dioxide photocatalytically-activated self-cleaning coating over a continuous glass float ribbon during the manufacture of the float ribbon comprising the steps of:

manufacturing a continuous glass float ribbon having a first major surface and an opposite major surface defined as a second major surface, the first major surface having a thin layer of a tin oxide diffused therein characteristic of forming the glass float ribbon on a molten tin bath;

positioning a chemical vapor deposition coating apparatus over the surface of the float ribbon at a point in the manufacture of the float ribbon where the float ribbon has a temperature of at least about 400°C (752°F);

directing a metal oxide precursor selected from the group consisting of titanium tetrachloride, titanium tetraisopropoxide and titanium tetraethoxide in a carrier gas stream through said chemical vapor deposition apparatus over the surface of the float ribbon and annealing the float ribbon to produce a titanium dioxide photocatalytically-activated self-cleaning coating over the glass float ribbon.

28. A method for providing a titanium dioxide photocatalytically-activated self-cleaning coating over a continuous glass float ribbon during the manufacture of the float ribbon comprising the steps of:

manufacturing a continuous glass float ribbon having a first major surface and an opposite major

surface defined as a second major surface, the first major surface having a thin layer of metal selected from the group consisting of tin, tin oxides and mixtures thereof diffused therein characteristic of forming the glass float ribbon on a molten tin bath;

depositing a photocatalytically-activated self-cleaning coating over at least one of the major surfaces by positioning a spray pyrolysis coating apparatus over the surface of the float ribbon at a point in the manufacture of the float ribbon where the float ribbon has a temperature of at least about 400°C (752°F), directing an aqueous suspension of titanyl acetylacetonate and wetting agent in an aqueous medium through said spray pyrolysis coating apparatus over the surface of the float ribbon and annealing the float ribbon in air to produce a titanium dioxide photocatalytically-activated self-cleaning coating over the glass float ribbon.

29. In a method for forming a glass float ribbon wherein the method includes the steps of melting glass batch materials in a furnace; delivering the molten glass onto a bath of molten tin; pulling the molten glass across the tin bath whereupon the glass is sized and controllably cooled to form a dimensionally stable glass float ribbon; removing the float ribbon from the tin bath; moving the float ribbon by conveying roller through a lehr to anneal the float ribbon; moving the float ribbon to a cutting station on conveying rollers where the ribbon is cut into glass sheets, the improvement comprising:

depositing a photocatalytically-activated self-cleaning coating over a surface of said float ribbon as the ~~float ribbon is formed.~~

30. The method of claim 29 wherein said photocatalytically-activated self-cleaning coating is deposited by a process selected from the group consisting of spray pyrolysis and chemical vapor deposition.

31. The method of claim 29, the improvement further comprising depositing a sodium ion diffusion barrier layer over a surface of said float ribbon and depositing said photocatalytically-activated self-cleaning coating over said sodium ion diffusion barrier layer.

32. A method for the manufacture of a photocatalytically-activated self-cleaning article of manufacture comprising the steps of:

providing an article of manufacture having at least one surface;

depositing a photocatalytically-activated self-cleaning coating over the surface of the article of manufacture by a process selected from the group consisting of chemical vapor deposition, magnetron sputtered vacuum deposition and spray pyrolysis.

33. The method of claim 32 wherein the article of manufacture is a glass sheet and said depositing step is performed during a process of modifying said glass sheet selected from the group consisting of bending and tempering of said glass sheet.

34. The method of claim 32 further comprising the step of depositing a sodium ion diffusion barrier layer over said surface and depositing said photocatalytically-activated self-cleaning coating over said sodium ion diffusion barrier layer whereupon said sodium ion diffusion barrier layer inhibits

migration of sodium ions from the surface of said article to said photocatalytically-activated self-cleaning coating.

35. The method of claim 34 wherein the sodium ion diffusion barrier layer is deposited by a process selected from the group consisting of chemical vapor deposition, spray pyrolysis and magnetron sputtered vapor deposition.

36. The method of claim 35 wherein said step of depositing the sodium ion diffusion barrier layer is performed during a process of modifying said glass sheet selected from the group consisting of bending and tempering of said glass sheet.

37. The method of claim 32 further comprising the step of annealing said photocatalytically-activated self-cleaning coating to increase a photocatalytic reaction rate of said photocatalytically-activated self-cleaning coating.

38. The method of claim 37 wherein said annealing step includes raising said photocatalytically-activated self-cleaning coating to a temperature of about 500°C for a time period of at least about 3 minutes and controllably cooling said photocatalytically-activated self-cleaning coating.

39. The method of claim 38 wherein said photocatalytically-activated self-cleaning coating has a photocatalytic reaction rate of at least about 2×10^{-3} $cm^{-1}min^{-1}$.

40. The method of claim 38 wherein said photocatalytic reaction rate is determined as the rate of removal of a stearic acid test film in the range of 100 to 200 Angstrom thick deposited over said photocatalytically-activated self-cleaning coating wherein said photocatalytic reaction rate

is quantitatively ~~determined as the slope of a curve formed~~ by a plotting of a plurality of Fourier Transform Infrared Spectrophotometer measurements of the integrated intensity of carbon-hydrogen stretching vibrational absorption bands of the stearic acid test film versus an accumulated time of exposure of said photocatalytically-activated self-cleaning coating to ultraviolet radiation of a frequency within the range of about 300 to 400 nanometers provided by an ultraviolet radiation source positioned over said photocatalytically-activated self-cleaning coating and having an intensity of about 20 watts per square meter as measured at the surface of the photocatalytically-activated self-cleaning coating.

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